Application of the equations-of-motion method to the excited states of N_2, CO, and C_2H_4*

John Rose, Tai-ichi Shibuya,† and Vincent McKoy‡
Arthur Amos Noyes Laboratory of Chemical Physics,§ California Institute of Technology, Pasadena, California 91109
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We have used the equations-of-motion method to study various states of N_2, CO, and ethylene. In this approach one attempts to calculate excitation energies directly as opposed to solving Schrödinger's equation separately for the absolute energies and wavefunctions. We have found that by including both single particle–hole and two particle–hole components in the excitation operators we can predict the excitation frequencies of all the low-lying states of these three molecules to within about 10% of the observed values and the typical error is only half this. The calculated oscillator strengths are also in good agreement with experiment. The method is economical, requiring far less computation time than alternative procedures.

I. INTRODUCTION

In previous papers we have discussed the equations-of-motion method as an approach to predicting the excitation energies and transition moments of electronic transitions of atoms and molecules. In these methods one attempts to calculate the excitation frequencies of a system directly as opposed to the more conventional approach of solving Schrödinger's equation separately for the energies and wavefunctions of the ground and excited states. In the equation-of-motion method (EOM) one calculates a set of amplitudes for each excited state which specify the relationship of that state to the ground state. These amplitudes are the components of an excitation operator and along with the excitation frequencies are the solution of the equations of motion. One of the specific advantages of this method is that the matrix elements needed to set up the equations should be very insensitive to the inaccuracies of the approximate ground state wavefunction used to evaluate them.

In this paper we discuss the results of calculations on nine low-lying states of CO and eleven states of N_2. The main purpose of these calculations is to test the accuracy and practicality of the equations-of-motion approach to studying the excited states of molecules. The results are very encouraging. For example, the predicted excitation frequencies of the nine states of CO all lie within 1% to 6% of the experimental values while those of N_2 are within 1 to 9% of experiment. The calculated intensities of the transitions are also in good agreement with experimental data. These results also support our statement that this approach to predicting excitation energies would be direct and economical. In fact the calculations reported in this paper required very modest computing time. We also report some more recent calculations on the vertical excitation in the N→V band of ethylene. Our results show that the vertical excitation energy of this transition is 7.9 eV and the oscillator strength is 0.40 assuming a Franck–Condon factor of unity. This is in very good agreement with the experimental results of 7.6 eV and 0.34 for the excitation energy and total oscillator strength, respectively.

In Sec. II we briefly discuss the final form of the equations of motion. Section III gives the results of our calculations on N_2, CO, and ethylene. We conclude the paper with a summary of our conclusions concerning the accuracy and practicality of the equations-of-motion method. These conclusions are quite optimistic. In the Appendix we give computational details including the composition of the atomic orbital basis sets used in these calculations.

II. THEORY

In this section we review some pertinent aspects of the solution of the equations of motion we have recently proposed. References 1 and 2 contain the necessary details. The variational form of the equations-of-motion states that the operator for generating an excited state $|\lambda\rangle$ from the ground state $|0\rangle$ is exactly a solution of the equation[2]

$$\langle 0|[\delta O_\lambda, H, O_\lambda^+]|0\rangle = \omega_\lambda \langle 0|[\delta O_\lambda, O_\lambda^+]|0\rangle, \quad (1)$$

where ω_λ is the excitation energy, $E_\lambda - E_0$, and the double commutator is defined by

$$2[A,H,B] = [A,[H,B]] + [[A,H],B]. \quad (2)$$

δO_λ is a variation on O_λ. The operator O_λ^+ is specified by a set of amplitudes which determine the relative importance of various particle-hole excitations in generating the state $|\lambda\rangle$, i.e.,

$$O_\lambda^+|0\rangle = |\lambda\rangle. \quad (3)$$

The dominant terms in O_λ^+ are the single particle–hole amplitudes (1p–1h). In the first approximation we restrict O_λ^+ to the 1p–1h form, and then we will include the 2p–2h contribution by a perturbation approach. Equation (1) gives the following equation[3] for the amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ and the excitation frequency ω_λ:

$$\begin{bmatrix} A(S) & B(S) \\ -B^*(S) & -A^*(S) \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix} = \omega(\lambda S) \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(\lambda S) \\ Z(\lambda S) \end{bmatrix}, \quad (4)$$

where the matrix elements of A, B, and D are

$$A_{m\gamma,n\delta}(S) \equiv \langle 0 \,|[C_{m\gamma}(SM), H, C_{n\delta}{}^{+}(SM)]| \, 0\rangle,$$
$$B_{m\gamma,n\delta}(S) \equiv -\langle 0 \,|[C_{m\gamma}(SM), H, C_{n\delta}(\bar{S}\bar{M})]| \, 0\rangle,$$
$$D_{m\gamma,n\delta}(S) \equiv \langle 0 \,|[C_{m\gamma}(SM), C_{n\delta}{}^{+}(SM)]| \, 0\rangle. \quad (5)$$

$C_{m\gamma}{}^{+}(SM)$ is a spin-adapted particle–hole creation operator, and m and γ specify a particle and a hole state, respectively. To evaluate the matrix elements in Eq. (5) we write an approximate ground state wavefunction,

$$|\, 0\rangle \approx N_0(1+U)|\, HF\rangle, \quad (6)$$

where

$$U = \tfrac{1}{2} \sum_{m\gamma,n\delta} \sum_{S} C_{m\gamma,n\delta}{}'(S) C_{m\gamma}{}^{+}(S0) C_{n\delta}{}^{+}(\bar{S}\bar{O}). \quad (7)$$

The approximate ground state wavefunction, $|\, 0\rangle$, of Eqs. (6) and (7) contains the main correlation effects for closed-shell systems.[4] We have recently shown that with $|\, 0\rangle$ of Eq. (6), the matrix elements of Eq. (5) are, to a very good approximation[1,5]

$$A_{m\gamma,n\delta}(S) = A_{m\gamma,n\delta}{}^{(0)}(S) + \delta_\gamma[T_{mn} - \tfrac{1}{2}(\epsilon_m + \epsilon_n - 2\epsilon_\gamma)\rho_{mn}{}^{(2)}] - \delta_{mn}[T_{\gamma\delta} - \tfrac{1}{2}(2\epsilon_m - \epsilon_\gamma - \epsilon_\delta)\rho_{\gamma\delta}{}^{(2)}],$$
$$B_{m\gamma,n\delta}(S) = B_{m\gamma,n\delta}{}^{(0)}(S) + (-1)^S S_{m\gamma,n\delta} + X_{m\gamma,n\delta}(S),$$
$$D_{m\gamma,n\delta} = \delta_{mn}\delta_{\gamma\delta} + \delta_{mn}\rho_{\gamma\gamma}{}^{(2)} - \delta_{\gamma\delta}\rho_{mn}{}^{(2)}. \quad (8)$$

The matrices $A^{(0)}$ and $B^{(0)}$ in Eq. (8) are the A and B matrices of the random phase approximation and the other terms in Eq. (8) are as follows:

$$S_{m\gamma,n\delta} = -\sum_{p\mu} \{V_{m\mu\delta p} C_{p\mu,n\gamma}(0) + V_{n\mu\gamma p} C_{p\mu,m\delta}(0)\},$$
$$T_{mn} = -\tfrac{1}{2} \sum_{q\mu\nu} \{V_{mq\mu\nu} C_{n\mu,q\nu}{}^{*}(0) + V_{\mu\nu nq} C_{m\mu,q\nu}(0)\},$$
$$T_{\gamma\delta} = \tfrac{1}{2} \sum_{pq\nu} \{V_{pq\gamma\nu} C_{p\delta,q\nu}{}^{*}(0) + V_{\delta\nu pq} C_{p\gamma,q\nu}(0)\}, \quad (9)$$
$$V_{ijkl} = \langle i(1) j(2)|\, 1/r_{12} \,|\, k(1) l(2)\rangle,$$
$$C_{ijkl}(0) = \tfrac{3}{2} C_{ijkl}{}'(0) - \tfrac{1}{2} C_{ijkl}{}'(1),$$
$$C_{ijkl}(1) = \tfrac{3}{2} C_{ijkl}{}'(1) - \tfrac{1}{2} C_{ijkl}{}'(0). \quad (10)$$

In Eqs. (8)–(10) the indices m, n, p, and q always refer to particle states and γ, δ, μ, and ν to whole states. The matrices T and S in (9) depend linearly on both the interaction elements V_{ijkl} and the correlation coefficients $C_{ijkl}{}'$. Only integrals of the form $V_{m\gamma n\delta}$ and $V_{mn\gamma\delta}$ are needed to compute the matrix elements in (8). The matrix X which contains interaction elements V_{mnpq} and $V_{\gamma\delta\mu\nu}$, which are not of this type, has been shown to be negligible and is not included in these calculations.[5] ϵ_m or ϵ_γ represents a Hartree–Fock (HF) orbital energy. $\rho_{mn}{}^{(2)}$ and $\rho_{\gamma\delta}{}^{(2)}$ are the second order density matrix corrections and depend quadratically on the correlation coefficients; terms containing them are part of the renormalization scheme.[6] If all correction coefficients $C_{ijkl}{}'(S)$ are ignored the elements of (8) reduce to the random phase approximation (RPA) matrices.

With these approximations to the matrix elements $A_{m\gamma,n\delta}$, $B_{m\gamma,n\delta}$, and $D_{m\gamma,n\delta}$, the equation of motion (4) can be solved by standard matrix algebra to yield the 1p–1h amplitudes $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ and the corresponding excitation energy ω_λ. Although the results given here are obtained from the solution of (4), accurate answers (see Appendix) can be obtained by including only diagonal terms in the D matrix, the principal advantage being that a new eigenvalue equation can be formed which has the same matrix form as the simple RPA.[2]

Equation (4) is the final form of the equations of motion for the excitation frequencies, $\omega(\lambda)$, in the single particle–hole approximation. In this approximation the excitation operator, $O_\lambda{}^{+}$, contains only 1p–1h creation and destruction operators, $C_{m\gamma}{}^{+}(SM)$ and $C_{m\gamma}(\bar{S}\bar{M})$, respectively. These excitations are from a correlated ground state. Note that the equations are designed so that the matrix elements needed are ground state expectation values of double commutators. These should depend on relatively simple properties of the wavefunction. Since these double commutators, e.g., $A_{m\gamma,n\delta}$ and $B_{m\gamma,n\delta}$, are of lower particle rank than matrix elements such as $\langle 0 \,|\, H \,|\, 0\rangle$ they are correspondingly less sensitive to the details of $|\, 0\rangle$. In principle one can solve Eq. (4) and the equation defining the ground state

$$O_\lambda |\, 0\rangle = 0 \qquad \text{for all } \lambda \quad (11a)$$

self-consistently. In Ref. 5 we showed that Eq. (11a) leads to the approximate conditions

$$Z_{m\gamma}(\lambda S) \cong \sum_{n\delta} C_{m\gamma,n\delta}{}^{*}(S)\, Y_{n\delta}(\lambda S). \quad (11b)$$

$C_{m\gamma,n\delta}$ is defined in Eq. (10). In practice Eq. (11) can be solved only approximately but this is a minor point since, as expected, the calculated excitation frequencies are not sensitive to small changes in the correlation coefficients $\{C_{m\gamma,n\delta}{}'\}$, Eq. (7). In the calculations presented here we solve (4) iteratively using the amplitudes $\{Y_{m\delta}\}$ and $\{Z(m\delta)\}$ in (11) to determine the correlation coefficients for a new iteration until the eigenvectors and eigenvalues have converged. However, an initial approximation to the coefficients $C_{ijkl}{}'$ using Rayleigh–Schrödinger perturbation theory gives essentially the converged result. Note that the particle–hole pairs $\{m\gamma\}$ determine the 2p–2h components which should be included in the ground state $|\, 0\rangle$.

Generally the most important compounds of low-lying excited states are the single-particle–hole pairs. In the complete expansion of the excitation operator $O_\lambda{}^{+}$, these would have the largest amplitudes. However doubly excited configurations (relative to the ground state)—two particle–hole components—can affect the excitation energies of some molecular states by more than 3 eV, the actual amount reflecting mainly a self-consistent readjustment of the core of basically ground-state (hole) orbitals during the excitation process. In Ref. 6 we showed how the theory including two-particle-like states is equivalent to the single-particlelike theory with a renormalized interaction and suggested a perturbation approximation for including their effects on

TABLE I. SCF molecular orbital eigenvalues for N_2.[a]

MO		ϵ_γ	MO		ϵ_m	MO		ϵ_m
1	$1\sigma_g$	−15.7079	8[b]	$3\sigma_u$	0.0257	20	$5\sigma_g$	0.8602
2	$1\sigma_u$	−15.7043	9	$1\pi_{gx}$	0.0910	21	$6\sigma_u$	1.0232
3	$2\sigma_g$	−1.5255	10	$1\pi_{gy}$	0.0910	22	$7\sigma_u$	1.5413
4	$2\sigma_u$	−0.7727	11	$4\sigma_u$	0.1632	23	$4\pi_{gx}$	1.6651
5	π_{ux}	−0.6240	12	$2\pi_{gx}$	0.1654	24	$4\pi_{gy}$	3.6651
6	π_{uy}	−0.6240	13	$2\pi_{gy}$	0.1654	25	$3\pi_{ux}$	3.0148
7	$3\sigma_g$	−0.6271	14	$2\pi_{ux}$	0.5320	26	$3\pi_{uy}$	3.0148
			15	$2\pi_{uy}$	0.5320	27	$8\sigma_u$	3.0819
			16	$4\sigma_g$	0.5460	28	$6\sigma_g$	3.3528
			17	$5\sigma_u$	0.5869	29	$5\pi_{gx}$	3.9962
			18	$3\pi_{gx}$	0.6114	30	$5\pi_{gy}$	3.9962
			19	$3\pi_{gy}$	0.6514	31	$9\sigma_u$	33.2482
						32	$7\sigma_g$	33.5275

[a] In a $\{[4s3p]+R(2p_z+2d\pi)_{CM}\}$ basis of contracted Gaussians. This basis gives $E_{SCF}=-108.888$ a.u. See the Appendix for details.
[b] Orbitals 8–13 are diffuse functions.

the excitation frequencies and transition moments. The main thrust of the argument is that if $\{Y_{m\gamma}\}$ and $\{Z_{m\gamma}\}$ are the amplitudes of the 1p–1h components in O_λ^+, then the excitation frequency of this transition is, to a good approximation,

$$\omega=\omega^{(1p-1h)}-\Delta\omega, \tag{12}$$

where $\omega^{(1p-1h)}$ is the excitation energy of the 1p–1h approximation, i.e., an eigenvalue of Eq. (4) and

$$\Delta\omega=\tilde{Y}^*\Delta_a\tilde{Y}+\tilde{Z}^*\Delta_d\tilde{Z}. \tag{13}$$

The elements of the matrices Δ_a and Δ_d are given explicitly in Eqs. (46) and (47) of Ref. 6, but they are essentially perturbationlike matrix elements in which the numerator is a matrix element of the Hamiltonian between a 1p–1h and 2p–2h component. The denominators are particle–hole energy differences. Actually the inclusion of 2p–2h terms can be viewed as consistent with an expansion of the equation of motion Eq. (4) to second order (see Appendix). We refer to the excitation frequencies of Eq. (12) as those of the equations of motion including 1p–1h and 2p–2h components.

Finally in the 1p–1h theory the transition moment matrix element between a state $|\lambda\rangle$ and the ground state $|0\rangle$ is given, to the same accuracy as Eq. (4) (to second order), as

$$M_{o\lambda}=\langle 0\,|\,M\,|\,\lambda\rangle=\sum_{m\gamma}[Y_{m\gamma}^*(\lambda)M_{m\gamma}+Z_{m\gamma}^*(\lambda)M_{m\gamma}], \tag{14a}$$

$$M_{m\gamma}=M_{m\gamma}^0+\sum_\delta M_{m\delta}^0\rho_{\gamma\delta}^{(2)}-\sum_n M_{n\gamma}^0\rho_{mn}^{(2)}. \tag{14b}$$

$M_{m\gamma}^0$ is the transition moment between a hole orbital γ and a particle orbital m, and $\rho_{mn}^{(2)}$ and $\rho_{\gamma\delta}^{(2)}$ are defined as in (8). The two last terms in Eq. (14b) represent second order corrections to $M_{o\lambda}$ and tend to alter (usually decrease) it by only a few percent. Other second order corrections due to 2p–2h components are not included here. They depend only on particle–particle (M_{mn}) and hole–hole ($M_{\gamma\delta}$) transition moments and should be of lesser magnitude. Many sum rules, including those for the oscillator strength and rotational strength, must be very nearly satisfied in this method.[7] In terms of $M_{o\lambda}$ the oscillator strength, f, of the transition is

$$f=\tfrac{2}{3}\Delta E M_{o\lambda}^2. \tag{15}$$

In the following sections we discuss the results of calculations on various states of N_2, CO, and C_2H_4 using the 1p–1h theory, Eq. (4), and the 1p–1h and 2p–2h theory, Eq. (12).

III. APPLICATIONS

A. States of N_2

The electron configuration of the ground state of N_2 is

$$(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^2(2\sigma_u)^2(\pi_{ux})^2(\pi_{uy})^2(3\sigma_g)^2.$$

We have considered the following states: $B\,^3\Pi_g(3\sigma_g\rightarrow\pi_g)$, $a\,^1\Pi_g$ $(3\sigma_g\rightarrow\pi_g)$, $A\,^3\Sigma_u^+$, $b\,^1\Sigma_u^+$, $B\,^3\Sigma_u^-$, $a'\,^1\Sigma_u^-$, $W\,^3\Delta_u$, and $w\,^1\Delta_u$ [all $(\pi_u\rightarrow\pi_g)$], $c'\,^1\Sigma_u^-(3\sigma_g\rightarrow 3\sigma_u)$, $C\,^3\Pi_u$ $(2\sigma_u\rightarrow\pi_g)$, and $b\,^1\Pi_u$ $(2\sigma_u\rightarrow\pi_g)$. We indicate in parentheses the electron configuration of the principal component of each state.

The first step of the calculation is to carry out a Hartree–Fock calculation in order to generate a particle–hole basis. The occupied orbitals are hole states and the virtual orbitals are particle states. The SCF calculations are done in a basis of Gaussian orbitals on each atom. The size of the basis determines the quality of the hole states and the number of particle states. We used a $[4s3p]$ basis of contracted Gaussian functions plus some diffuse components; details are given in the Appendix. Table I lists the hole and particle energy levels used in the calculation.

We include excitations out of all hole levels except the $1\sigma_g$ and $1\sigma_u$ levels. These levels are too low to have any effect on the low-lying excited states we consider. All particle–hole excitations of the appropriate sym-

TABLE II. Equations-of-motion calculations: excited states of N_2.[a]

State	N[b]	ΔE[c] (1p–1h)	ΔE[c] (1p–1h)+(2p–2h)	Exptl[c]	% Error[d]
$B\ ^3\Pi_g(3\sigma_g\rightarrow\pi_g)$[e]	15	9.6	7.5	8.1[f]	7
$a\ ^1\Pi_g$[g]	15	11.5	8.8	9.3	5
$A\ ^3\Sigma_u^+(\pi_u\rightarrow\pi_g)$	20	8.4	7.8	7.8	~0
$B'\ ^3\Sigma_u^-$[h]		11.3	10.2	9.7	6
	8				
$W\ ^3\Delta_u$		10.1	9.4	8.9[i]	6
$a'\ ^1\Sigma_u^-$		11.3	10.6	9.9	6
	8				
$\omega\ ^1\Delta_u$		12.0	11.0	10.3	6
$b'\ ^1\Sigma_u^+$		16.8	15.0	14.4[j]	4
	20				
$c'\ ^1\Sigma_u^+(3\sigma_g\rightarrow\sigma_u)$		15.5	12.1	12.9	6
$C\ ^3\Pi_u(2\sigma_u\rightarrow\pi_g)$	10	13.3	10.8	11.1	4
$b\ ^1\Pi_u$	10	17.4	14.0	12.8	9

[a] All calculations done at an equilibrium internuclear distance of 2.068 a.u.

[b] Number of single particle–hole pairs used in the calculation. See Appendix for discussion of the basis set and selection of the particle–hole excitations.

[c] In electron volts.

[d] Relative to the experimental value.

[e] Indicates the main component of the excitation relative to the ground state.

[f] The experimental results for this state and for the $a\ ^1\Pi_g$, $A\ ^3\Sigma_u^+$, $B\ ^3\Sigma_u^-$, $a'\ ^1\Sigma_u^-$, $\omega\ ^1\Delta_u$, and $C\ ^3\Pi_u$ states are those reported by W. Benesch, J. T. Vanderslice, S. G. Tilford, and P. G. Wilkinson, Astrophys. J. **142**, 1227 (1965). Their tabulations are based on high resolution optical data.

[g] Same designation as in the previous state.

[h] The next five states have the same principal 1p–1h component type.

[i] W. Benesch and K. A. Saum, J. Phys. B **4**, 732 (1971).

[j] The experimental results for the $b'\ ^1\Sigma_u^+$, $C\ ^3\Pi_u$, and $b\ ^1\Pi_u$ states are from the electron energy-loss spectrum of Ref. 10.

metry are included in the calculation on each state. These particle–hole pairs, in turn, determine the pair correlations—2p–2h components of the correlated ground state—which are included in the correlation function U of Eq. (7). From Eq. (4) it would seem that if N particle–hole pairs are included then the resulting equations give an unsymmetric $2N\times2N$ matrix. It is well known, however,[8] that the eigenvalue, ω, can be found by solving an $N\times N$ matrix for the eigenvalue ω^2. The largest matrices which we have to handle are, on the average, of dimensionality 25×25 to 30×30. With the 1p–1h pairs specified, Eq. (4) and Eq. (11b) can then be solved for the excitation frequencies in the 1p–1h approximation. These eigenvalues are the approximate excitation energies of the excited states of the system under the condition that these excited states differ only by single particle–hole excitations relative to a correlated ground state. In the next stage of the calculation we introduce the effect of 2p–2h excitations out of the correlated ground state. We include this effect by using the approximate results, Eq. (13), for the energy lowering of the 1p–1h frequency, due to these 2p–2h components. For each state all 2p–2h excitations derivable from the set of single particle–hole excitations i.e., $\{C_{m\gamma}^+\}$ are included.

Table II shows the results of calculations on eleven states of N_2. All these calculations were done at the ground state equilibrium internuclear distance of 2.068 a.u. In the first column we list the symmetry and the conventional spectroscopic designation of the various states. The next column shows the number of single particle–hole pairs used in setting up the equations of motion. The excitation frequencies in the 1p–1h approximation are listed in the third column. Comparison with the experimental vertical excitation energies show that this approximation predicts all the states to lie about 1 to 3 eV above the experimental values. Inclusion of 2p–2h components lowers the 1p–1h excitation frequencies by about 1 to 3 eV resulting in excitation energies in good agreement with the experimental values. The percentage errors of calculated excitation energies relative to the experimental values are in the range of 1% to 9% with an average error of about 5%. The experimental results are probably reliable to within a few percent while we believe that the various approximations made in deriving the final equation may lead to an error of the same order. We do not intend to make any extensive comparisons between our calculated values and those obtained by other methods, e.g., SCF or CI calculations. The prime

TABLE III. Oscillator strengths for transitions in N_2.

Transition	f_{el} [a]	$q_{v'v''}$ [b]	$f_{el}q_{v'v''}$	Exptl
$X\,^1\Sigma_g^+ \rightarrow c'\,^1\Sigma_u^+$	0.11	$q_{00}\sim 1$[c]	0.11	0.14 ± 0.04[d] 0.16[e]
$X\,^1\Sigma_g^+ \rightarrow b\,^1\Pi_u$	0.32	...	...	<0.3[f]
$X\,^1\Sigma_g^+ \rightarrow b'\,^1\Sigma_u^+$	0.49	...	...	Large "measured" f_{el} [g]

[a] $f_{el}=\frac{2}{3}\Delta E M^2$, where M is the dipole transition matrix element. The oscillator strengths in this column do not include any Franck–Condon factors.

[b] Franck–Condon factors for the v' and v'' levels.

[c] Reference 9.

[d] This is the measured f value for the 0–0 transition. See Ref. 9.

[e] Total f value from lifetime measurements by J. E. Hesser, J. Chem. Phys. **48**, 2518 (1968).

[f] See text. This is an estimate derived from the band oscillator strength measurements by the authors of Ref. 9.

[g] Weak due to intensity perturbations by $v'=5$ and 6 of the $c'\,^1\Sigma_u^+$ and $v'=0$ of the $e'\,^1\Sigma_u^+$ states. From shock-heated vibrationally excited N_2, $f_{el}(v''=5\rightarrow v'=2)\approx 0.83$ and $f_{el}(v''=8\rightarrow v'=2)\approx 0.4$ [J. P. Appleton and M. Steinberg, J. Chem. Phys. **46**, 1521 (1967)].

purpose of our calculations is to test the practicality and accuracy of the equations-of-motion method. The total amount of computing time is quite low. The calculations on all eleven states of N_2 required only about 20 min on an IBM 370/155. A typical breakdown of this time would be: 30% for the HF calculation on the ground state, 45% for the 1p–1h calculation, and 25% for the inclusion of the 2p–2h components. The other caulculations reported here, i.e., on CO and C_2H_4, both required less than twice this time.

In Table III we compare the calculated oscillator strenths with available experimental results. The calculated oscillator strengths in the second column of Table III do not contain any Franck–Condon factors. For transitions between states with very similar equilibrium internuclear distances and in the absence of perturbations by the vibrational levels of other states, we can expect the Franck–Condon factor for the 0–0 transition to be very close to unity. This is the case for the transition $X\,^1\Sigma_g^+$–$c'\,\Sigma_u^+$. Assuming a Franck–Condon (FC) factor of unity our calculated oscillator strength of 0.11 is in very good agreement with the measured values which lie in the range 0.14 ± 0.04.[9] It is well known that it is difficult to estimate FC factors for the X–$b\,^1\Pi_u$ transition because of strong perturbations of the vibrational levls of the $b\,^1\Pi_u$ well by those of the $c\,^1\Pi_u$ well.[9] However we can show that the calculated vertical electronic oscillator strength of 0.32 for the $X\rightarrow b\,^1\Pi_u$ is in good agreement with available experimental data. Geiger and Schoeder's[10] high resolution electron energy-loss spectrum shows[9] that the 965 Å band (12.84 eV), the 0–4 component of the $X\rightarrow b\,^1\Pi_u$ transition, accounts for 14% of the dipole oscillator strength in the 11.4–13.6 eV range. From their measured absolute value of $f(965\text{ Å})=0.055$, Lawrence *et al.*[9] could then show that the total dipole oscillator strength for the 11.4–13.6 eV region of the spectrum is 0.40. Almost all the intensity in this region of the spectrum comes from the $c'\,^1\Sigma_u^+$, $b\,^1\Pi_u$, and $c\,^1\Pi_u$ transitions. But the measured contribution of the $c'\,^1\Sigma_u^+$ state to the total f value is 0.14 ± 0.04 and hence the total f value of the $b\,^1\Pi_u$ and $c\,^1\Pi_u$ states lies between 0.22 and 0.30.[11] The $X\rightarrow b\,^1\Pi_u$ transition accounts for a large fraction of this total.[12] This is in agreement with our calculated value of 0.32 for the $X\rightarrow b\,^1\Pi_u$ transition if we assume a constant transition moment and sum over the whole band.

Finally we obtain a vertical electronic oscillator strength of 0.49 for $X\,^1\Sigma_g^+\rightarrow b'\,^1\Sigma_u^+$ transition. There are no reliable measured values for this transition. However the data of Ref. 10 shows that the intensity of this vertical transition is very low indicating that the effective FC factor for the transition is small. This is probably due to intensity perturbations of the $b'\,^1\Sigma_u^+$ levels by those of the $c'\,^1\Sigma_u^+$.

B. States of CO

The electron configuration of the ground state of CO is

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(1\pi)^4(5\sigma)^2.$$

We have done calculations on these states: $a\,^3\Pi(5\sigma\rightarrow 2\pi)$ $A\,^1\Pi(5\sigma\rightarrow 2\pi)$, $a'\,^3\Sigma^+$, $c\,^3\Sigma^-$, $I\,^1\Sigma^-$, $d\,^3\Delta$, $D\,^1\Delta$ [all $(1\pi\rightarrow 2\pi)$], $B\,^1\Sigma^+$ $(5\sigma\rightarrow\sigma)$, and $C\,^1\Sigma^+$ $(5\sigma\rightarrow\sigma)$. The electron configuration of the principal component of each stste is shown in parentheses. All calculations were done at an internuclear distance of 2.132 a.u. Table IV shows the hole and particle energy levels used in the calculation. The basis set used in the calculation is described in the Appendix.

Table V shows the results of calculations on nine states of CO. In the first column we list the symmetry and the conventional spectroscopic designation of the various states. The number of particle–hole pairs used in each calculation is listed in the next column. In the third and fourth column we show the calculated vertical excitation energies. The results in the third column are those in which only 1p–1h excitations out of the ground state are included in the excitation operator O_λ^+. As in the results for N_2 the exitation energies in this approximation are about 1 to 2 eV above the experimental values. Inclusion of 2p–2h components lowers these values leading to calculated excitation energies in good agreement with experiment. These results and the experimental values are shown in Columns 4 and 5, respectively, of Table V. The percentage errors of calculated excitation energies relative to the experimental values are in the range of 1% to 6% with an average error of about 3%. In terms of computer requirements the method is quite economical. For example the largest matrices involved are the order of 30×30. Calculations

TABLE IV. SCF molecular orbital eigenvalues for CO.[a]

MO		ϵ_γ	MO		ϵ_m	MO		ϵ_m
1	1σ	−20.6903	8[b]	6σ	0.0711	19	$4\pi_y$	0.8402
2	2σ	−11.3945	9	7σ	0.0817	20	12σ	0.8784
3	3σ	−1.5665	10	$2\pi_x$	0.1198	21	13σ	1.1629
4	4σ	−0.8006	11	$2\pi_y$	0.1198	22	14σ	1.7874
5	$1\pi_x$	−0.6493	12	8σ	0.1639	23	15σ	2.2186
6	$1\pi_y$	−0.6493	13	9σ	0.2990	24	$5\pi_x$	2.1089
7	5σ	−0.5594	14	$3\pi_x$	0.4109	25	$5\pi_y$	2.1089
			15	$3\pi_y$	0.4109	26	$6\pi_x$	4.0880
			16	10σ	0.4376	27	$6\pi_y$	4.0880
			17	11σ	0.7686	28	16σ	4.4496
			18	$4\pi_x$	0.8402	29	17σ	23.8040
						30	18σ	32.3068

[a] In a $\{[4s3p]+R(p_s+s)\}$ basis of contracted Gaussians. This basis gives $E_{SCF}=-112.6986$ a.u. See the Appendix for details.
[b] Orbitals 8, 9, 12, and 13 are diffuse functions.

using other methods have been carried out on various states of CO.[13] We do not want to make extensive comparisons between our values and those of other methods since we primarily want to test the practicality of our method. We note however that our calculated excitation energies are in as good—in many cases better—agreement with experiment as those of the CI calculations of Ref. 13. The CI calculations involve much larger matrices than those in the equations-of-motion method.

In Table VI we compare our calculated oscillator strengths with available experimental data. The $X\,^1\Sigma^+ \rightarrow A\,^1\Pi$ transition has been extensively studied by electron energy-loss spectroscopy. Lassettre *et al.*[14]

TABLE V. Equations-of-motion calculations: excited states of CO.[a]

State	N[b]	ΔE[c] (1p–1h)	ΔE[c] (1p–1h)+(2p–2h)	Exptl[c]	% Error[d]
$a\,^3\Pi(5\sigma\rightarrow 2\pi)$[e]	22	7.1	6.0	6.3[f]	3
$A\,^1\Pi$	22	10.3	8.5	8.4	~0
$a'\,^3\Sigma^+(1\pi\rightarrow 2\pi)$	30	9.3	7.9	8.4	6
$e\,^3\Sigma^-$[g]		11.5	9.5	9.7	2
	8				
$d\,^3\Delta$		10.5	8.9	9.2	3
$I\,^1\Sigma^-$		11.5	9.8	9.9	1
	8				
$D\,^1\Delta$		12.0	10.0	10.5	5
$B\,^1\Sigma^+(\sigma\rightarrow\sigma^*)$		13.8	11.4	10.8	6
	30				
$C\,^1\Sigma^+(\sigma\rightarrow\sigma^*)$		13.4	11.4	11.4	~0

[a] All calculations done at an equilibrium internuclear distance of 2.132 a.u.
[b] Number of single particle–hole pairs used in the calculation. See the Appendix for a discussion of the basis set and selection of the particle–hole excitations.
[c] In electron volts.
[d] Relative to the experimental value.
[e] Indicates the main component of the excitation relative to the ground state.
[f] The experimental results for the $A\,^1\Pi$, $B\,^1\Sigma^+$, and $C\,^1\Sigma^+$ states are from the electron energy-loss spectrum of V. Meyer, A. Skerbele, and E. Lassettre, J. Chem. Phys. **43**, 805 (1965). The experimental results for the other states are from G. Herzberg, T. Hugo, S. Tilford, and J. Simmons, Can. J. Phys. **48**, 3004 (1970).
[g] The next four states have the same principal component.

TABLE VI. Oscillator strengths for transitions in CO.

Transition	f_{el} [a]	$q_{v'v''}$ [b]	$f_{el}q_{v'v''}$	Exptl
$X\,^1\Sigma^+ \rightarrow A\,^1\Pi$	0.11	$q_{20} \approx 0.24$[c]	0.026	0.043[d] 0.15[e]
$X\,^1\Sigma^+ \rightarrow C\,^1\Sigma^+$	0.12	$q_{00} \sim 1$[f]	0.12	0.16[g]
$X\,^1\Sigma^+ \rightarrow B\,^1\Sigma^+$	0.048	$q_{00} \sim 1$[f]	0.048	0.016[g]
$X\,^1\Sigma^+ \rightarrow B$ and $C\,^1\Sigma^+$			0.17	0.18[h]

[a] $f_{el} = \frac{2}{3}\Delta E M^2$ where M is the dipole transition matrix element. The oscillator strengths in this column do not include any Franck–Condon factors.

[b] Franck–Condon factors for the v' and v'' levels.

[c] P. H. Krupenie, Natl. Std. Ref. Data Ser., Natl. Bur Std. (U.S.) **5**, (1966).

[d] This is the measured value for the $v'=0 \rightarrow v''=2$ transition. See Ref. 13.

[e] This is the total f value for the transition (see Ref. 14). This value takes into account the r-centroid dependence of the electronic transition moment. See text. Lassettre[13] obtains 0.19 from electron impact studies.

[f] See Ref. 14.

[g] Electron impact studies of Lassettre.[14]

[h] This is the total f value for the $X \rightarrow B$ and $X \rightarrow C$ transitions. See text for discussion.

obtained a value of 0.043 for the $v'=2$ level of $A\,^1\Pi$ state by extrapolating the generalized oscillator strength to zero momentum transfer. The calculated value of 0.026 for this transition is fair agreement with their result.[14] The total f value for the $X\,^1\Sigma^+ \rightarrow A\,^1\Pi$ transition obtained from lifetime measurements[15] is 0.15. To obtain this value they[15] included the r-centroid dependence of the electronic transition moment in analyzing Hesser's lifetime measurements.[16] If this dependence is neglected the total f value for the transition is about 0.094.[16] Our calculated estimate of 0.11 for the total f value of this transition—assuming a constant electronic transition moment for transitions to the $v'=0 \rightarrow v'=6$ levels—is in the range of these measured values, i.e., 0.09–0.15.

Finally the calculated f value of 0.12 for the $X \rightarrow C$ transition is in good agreement with the measured value of 0.16. This value is obtained by extrapolating the generalized oscillator strength to zero momentum transfer.[14] The agreement for the $X \rightarrow B$ transition is not as good. The calculated value is 0.048 while Lassettre's extrapolation of his electron-impact results gives 0.016. These transitions are quite close to each other with the B state lying 0.6 eV below the C state. Their data[14] also shows that the Born approximation is not valid for the $X \rightarrow B$ transition even at incident electron energies of $\mu 00$ eV.[17] Note that the calculated total f value for the $X \rightarrow B$ and $X \rightarrow C$ transitions is 0.17, in good agreement with their measured value of 0.18. To study these measurements more closely we plan to calculate the generalized oscillator strength as a function of momentum transfer in the Born approximation using the equations-of-motion method. Similar calculations on electron–helium scattering by Schneider have given accurate results.[18]

C. The T and V States of Ethylene

We have done additional calculations on the T and V states of ethylene which are the triplet and singlet states arising primarily from a $\pi \rightarrow \pi^*$ transition. In these calculations we use an extensive Gaussian atomic orbital basis with diffuse π^* components which is described in the Appendix. In a previous publication[5] we studied these same transitions in a smaller basis but we made two restrictive approximations in solving Eq. (4). First we included only those correlation coefficients in Eq. (7) made up of particle–hole pairs of the same symmetry as the excited state under study, in this case[19] B_{3u}. In this approximation we assumed that off-diagonal correlation coefficients were small so that

TABLE VII. SCF molecular orbital eigenvalues for C_2H_4.[a]

MO		ϵ_λ	MO		ϵ_m	MO		ϵ_m
1	$1a_{1g}$	−11.2420	9[b]	$2b_{1u}$	0.0088	21	$3b_{2u}$	0.4351
2	$1b_{3u}$	−11.2405	10	$1b_{2g}$	0.0122	22	$2b_{1g}$	0.4545
3	$2a_{1g}$	−1.0397	11	$3b_{1u}$	0.0392	23	$5b_{1u}$	0.6580
4	$2b_{3u}$	−0.7969	12	$2b_{2g}$	0.0456	24	$3b_{1g}$	0.7048
5	$1b_{2u}$	−0.6565	13	$3b_{2g}$	0.1141	25	$5b_{2g}$	0.7150
6	$3a_{1g}$	−0.5812	14	$4b_{1u}$	0.1503	26	$6a_{1g}$	0.7325
7	$1b_{1g}$	−0.5197	15	$4b_{2g}$	0.2124	27	$5b_{3u}$	0.8911
8	$1b_{1u}$	−0.3731	16	$3b_{3u}$	0.2607	28	$6b_{3u}$	1.1294
			17	$4a_{1g}$	0.2862	29	$7a_{1g}$	1.3051
			18	$2b_{2u}$	0.3838	30	$4b_{2u}$	1.4115
			19	$4b_{3u}$	0.4004	31	$7b_{3u}$	1.4406
			20	$5a_{1g}$	0.4177	32	$4b_{1g}$	1.7326
						33	$8a_{1g}$	23.7659
						34	$8b_{3u}$	24.0592

[a] In a $\{[4s2p/2s]+R(3p_xC)\}$ basis of contracted Gaussians. This basis gives $E_{SCF} = -78.0111$ a.u. See the Appendix for details.

[b] Orbitals 9–14 are diffuse functions.

TABLE VIII. The $N \rightarrow T$, $N \rightarrow V$, and $N \rightarrow R'''$ transitions of C_2H_4.[a]

Transition	N [b]	ΔE [c] (1p–1h)	ΔE [c] (1p–1h)+(2p–2h)	ΔE [c] Exptl	$\langle \pi^* \mid z^2 \mid \pi^* \rangle$[d]	f_{calc} [e]	f_{obs}
$N \rightarrow T$	22	4.8	4.1	4.6	2.7	...	...
$N \rightarrow V$		9.0	7.9	7.6[f]	9.0	0.40	0.34[g]
	22						
$N \rightarrow R'''$		10.4	8.9	9.05[h]	83.3	0.02	0.002–0.01[i]

[a] Calculations are all done at approximately the ground state geometry (C–C bond length of 1.35 Å, C–H bond length of 1.07 Å, CH–C–H of 120°).

[b] Number of 1p–1h pairs used in the calculation.

[c] In electron volts.

[d] The average value of z^2 (perpendicular to the molecular plane) for the π^* orbital [in $(\text{a.u.})^2$].

[e] Assuming a Franck–Condon factor of unity for the vertical excitation.

[f] Maximum in the $N \rightarrow V$ absorption.

[g] Total f value for the transition.

[h] This is the $N \rightarrow R'''$ transition in Wilkinson's assignment. See text and Ref. 20 for discussion.

[i] Preliminary results of Allan Smith and Barney Ellison (Yale University). See text for discussion.

$C_{m\gamma,n\delta}'(0) = C_{m\gamma,n\delta}(1)$. Secondly, we did not use the fully renormalized matrix elements of Eq. (8), which include terms quadratic in the coefficients $C_{m\gamma,n\delta}'$. These terms are of the same order as other terms linear in $C_{m\gamma,n\delta}'$ and an interaction matrix element V_{ijkl}. These assumptions, which work reasonably well for ethylene, are poor when applied to systems with stronger electron correlation in the ground state, especially for states of symmetries that are unimportant in the correlation function, Eq. (7), e.g., in diatomic molecules. For consistency we now solve the equations of motion without these assumptions. The magnitude of these corrections is discussed in the Appendix; although they are small the effect is significant enough that these results are not directly comparable with those of Ref. 5. Table VII lists the particle and hold energy levels used in these calculations.

Table VIII shows the excitation energies for the $N \rightarrow T$, $N \rightarrow V$, and $N \rightarrow R'''$ transitions. The $N \rightarrow R'''$ transition is the first member of the $N \rightarrow nR'''$ Rydberg series according to Wilkinson's assignment.[20] Wilkinson[20] suggested that this R''' series arose from a $\pi \rightarrow nd\pi_x$ transition. This Rydberg state is of the same symmetry as the V state. As in the results on N_2 and CO we see that the excitation energies obtained by including only 1p–1h components are larger than the experimental values but when 2p–2h components are included theory and experiment are in agrement. The excitation energies for the T and V states are 4.1 and 7.9 eV compared with the observed values of 4.6 and 7.6 eV, respectively.[21] The calculated oscillator strength for the vertical transition is 0.40 compared with the experimental total f value of 0.34 for the $N \rightarrow V$ band.[22,23] Our results also show that the π^* orbital of the V state, although somewhat more diffuse than the π^* orbital of the T state, is a valencelike molecular orbital. A valencelike π^* molecular orbital is consistent with most available experimental information on the $N \rightarrow V$ band. Previous calculations, in both the HF [24] and limited configuration interaction approximation,[25] have given a singlet-state with a diffuse π^* orbital as the lowest state of this symmetry. In the case of the HF calculations it is very probable that in the SCF approximation the lowest state is in fact a Rydberg state. An extensive configuration interaction calculation should give results similar to those of Table VIII, e.g., a valencelike $\pi \rightarrow \pi^*$ state at about 7.8–8.0 eV.[26] An important consideration in such a calculation would be the inclusion of enough valencelike virtual orbitals to properly describe sigma–pi correlations in addition to diffuse functions, leading to a very large matrix problem.

In Table VIII we also list the excitation energy and oscillator strength for the first $\pi \rightarrow nd\pi_x$ Rydberg state. The calculated excitation energy of 8.9 eV is in good agreement with the value reported by Wilkinson[20] for this Rydberg transition. Wilkinson[20] suggested that the state at 9.05 eV was the first member of a $N \rightarrow R'''$ Rydberg series involving a $\pi \rightarrow nd\pi_x$ transition. This region of the spectrum has recently been remeasured.[22] Our results are in fair agreement with these experimental results and with those of Wilkinson.[20]

IV. CONCLUSIONS

We have used the equations-of-motion method to study various states of N_2, CO, and ethylene. In this approach one attempts to calculate excitation energies directly as opposed to solving Schrödinger's equation separately for the absolute energies and wavefunctions. The main purpose of these calculations is to test the accuracy and practicality of the methods. We have found that by including both single particle–hole and two particle–hole components in the excitation operators we can predict the excitation frequencies of all the low-lying states of these three molecules to within about

10% of the observed values and the typical error is only half this. The calculated oscillator strengths are also in good agreement with experiment. The method is economical requiring far less computation time than a comparable configuration interaction study or self-consistent field iterative procedures. We believe the EOM method will give equally accurate results for any molecule whose ground state is well represented by the Hartree–Fock scheme.

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APPENDIX: DETAILS OF THE SOLUTION OF THE EOM

Although the "equation of motion" (1) is exact in principle, it must be truncated in any practical calculation. Errors can occur through limiting the basis set and the set of MO's used in the calculation or in the formal expansion of (1). This latter difficulty does not occur in a *complete* CI calculation but restricting the configurations included amounts to a similar but more arbitrary approximation. The expansion to "second order" used in obtaining (4) is consistent with a type of perturbation theory at least from a heuristic point of view, as is the derivation of the Eq. (13) for 2p–2h corrections. The resulting matrix equations are of low dimensionality even when an extensive basis set must be employed.

In second quantization formalism the many electron Hamiltonian can be written as

$$H=H_1+H_2+H_3, \tag{A1}$$

where

$$H_1=\sum_i \epsilon_i n_i,$$

$$H_2=-\sum_{i\gamma}(2J_{i\gamma}-K_{i\gamma})n_i+\tfrac{1}{2}\sum_{ij}(J_{ij}-K_{ij})n_i + \sum_{ij}K_{ij}C_{ij}^{+}(00)C_{ji}^{+}(00),$$

$$H_3=-\sum_{ij}(1-\delta_{ij})\Big[\sum_j(2V_{i\gamma j\gamma}-V_{i\gamma\gamma j})+\tfrac{1}{2}\sum_k V_{ikkj}\Big]\sqrt{2} \times C_{ij}^{+}(00)+\sum_{ijkl}(1-\delta_{ik}\delta_{jl})(1-\delta_{il}\delta_{jk}) \times V_{ijkl}C_{ik}^{+}(00)C_{jl}^{+}(00),$$

$$J_{ij}=V_{ijij},$$

$$k_{ij}=V_{iijj},$$

$$n_i=\sqrt{2}C_{ii}^{+}(00).$$

The notation is the same as in the test with J_{ij} and K_{ij} being Coulomb and exchange integrals and n_i being a space orbital number operator. In the Rayleigh–Schrödinger perturbation scheme H_1 is the zero order Hamiltonian H_0, and H_2 and H_3 are the diagonal and off-diagonal terms of the perturbation H'. Grimaldi[27] has shown that this perturbation scheme gives accurate correlation coefficients for the ground states of N_2 and CO using only second order energy corrections. A reasonable approach to solving (1) would then be to consider the correlation coefficients C_{ijkl}' as first order terms since they are first order corrections to the ground state wavefunction. Expansion (4) then includes all terms of the form $(V_{ijkl})^m(C_{ijkl}')^n$, where $m+n\leq 2$, and is thus analogous to a Rayleigh–Schrödinger expansion of the excitation energy through second order. Similar arguments can be made for dropping interaction terms in the double excitation matrix elements. Use of another scheme such as chosing the zero order Hamiltonian as H_1+H_2 of (A1) would be more difficult to implement. Furthermore we find that the discrepancy between the eigenvalues obtained in these two schemes would be less than about 5% if double excitations are handled consistently. However it can be much greater if only the (1p–1h) theory is used.

Of the various approximations made in the previously published scheme[5] (summarized in Sec. III.C in text) only the one which involves setting $C_{ijkl}'(0)=C_{ijkl}'(1)$ is exceptionally poor. Although this is true identically if $i=k$ or $j=l$ the difference for the smaller off-diagonal coefficients is important since singlet and triplet excitation frequnecies are affected predominately by the singlet or triplet coefficients, respectively. Thus the T state of ethylene, which should be adequately described by the $[3s2p/1s]$ basis of Ref. 5, decreases in energy by 0.9 eV when the present expanded basis is used in the original scheme.[5] However, when calculations are done in both bases using the correct equations (8), the charge is only 0.2 eV. The idea of including only correlation coefficients generated from the same symmetry as the excitation under consideration is reasonable if these represent a large portion of the correlation energy, e.g., 60% in the case of the B_{3u} symmetry of ethylene. Inclusion of all the coefficients increases the B_{3u} frequencies by less than 0.4 eV. In N_2 or CO there are many low-lying states of different symmetries and all the coefficients must be included.

Renormalization of the equations as outlined in Ref. 6 involves inclusion of terms in the second order correction to the matrix A which are proportional to the second order density matrix and also inclusion of the matrix D. These effects tend to cancel causing a typical excitation frequency of a valence state to decrease less than 5%. The greatest effect was found for the $a\,^3\Pi$ state of CO where renormalization decreased the frequency by 8%. Treating D as diagonal is a very good approximation affecting the frequencies by less than 1%.

Finally iterating the solutions to self-consistency is of minor importance. One iteration is sufficient to converge the frequencies to the final answer which, in N_2 or CO,

is only about 0.1 eV or less above that using the initial (Rayleigh–Schrödinger) correlation coefficients C_{ijkl}'. In accordance with these observations, an argument could be made for not iterating the solutions to self-consistency. In ethylene the T and V states increase in energy about 0.2 eV upon iteration, and at convergence sigma–pi correlation is larger and pi correlation is smaller relative to the Rayleigh–Schrödinger guess.

The basis sets used in these calculations contain both valence and diffuse s and p contracted Gaussian functions. d functions are relatively unimportant, affecting the frequencies by several tenths of an electron volt in N_2 for instance. The contracted valence functions were those of Dunning.[28] For ethylene we used the $[4s2p/2s]+R(3p_zC)$ basis. The diffuse $p\pi$ functions on the carbon atoms have exponents $\zeta=0.0365$, 0.0116, and 0.0037. For CO the basis is a $[4s3p]$ valence set plus a single diffuse s function on carbon and oxygen ($\zeta=0.036$ and $\zeta=0.048$) and a diffuse p_z function on each center ($\zeta=0.030$ and 0.040). In N_2 we used a $[4s3p]$ valence basis plus two p_z functions ($\zeta=0.05$ and 0.01) and two $d\pi$ functions ($\zeta=0.3$ and 0.03) at the center of the molecule. This is necessary to describe the $c'\,{}^1\Pi_u{}^+$, $b'\,{}^1\Sigma_u{}^+$, and $b\,{}^1\Pi_u$ states. The importance of diffuse functions in the final frequency ranges from about 0.3 eV for the V state of ethylene and 1.5 eV for the b' state of N_2 to several electron volts for the c' state of N_2 and the B and C states of CO. All these states are somewhat diffuse. It is not usually necessary to use as large a valence basis as those above. For CO a $[3s2p]$ basis contracted from a $[7s3p]$ basis[29] with diffuse functions yields almost identical excitation energies as the $[4s3p]$ basis. However the integral and SCF calculations require only a fraction of the time. The diffuse functions must be used as they possibly supplement the smaller valence basis in describing valence states.

In practice we have taken only the lowest 19 virtual orbitals in solving the equations of motion for N_2 and CO. Only for the $^1\Sigma^+$ states of CO was it necessary to further truncate the particle–hole basis (from 32 to 30) to utilize existing programs. Neither truncation has a significant effect on the excitation energies since representative valence and diffuse virtual orbitals are included accounting for about half the total ground state correlation energy. For ethylene we used a more efficient transformation program which included 22 of 26 virtual orbitals. To keep the total cost of a calculation small for molecule of low symmetry reasonable—let us say under 1 hr—it is necessary at present to restrict the total number of MO's to about 30.

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† Present address: Department of Physics, University of the Pacific, Stockton, Calif.

‡ Alfred P. Sloan Foundation Fellow.

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